

Surface-directed spinodal decomposition: A molecular dynamics study

Prabhat K. Jaiswal,¹ Sanjay Puri,¹ and Subir K. Das²

¹*School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110 067, India*

²*Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India*

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We use molecular dynamics simulations to study surface-directed spinodal decomposition in unstable binary AB fluid mixtures at wetting surfaces. The thickness of the wetting layer R_1 grows with time t as a power law ($R_1 \sim t^\theta$). We find that hydrodynamic effects result in a crossover of the growth exponent from $\theta \simeq 1/3$ to 1. We also present results for the layerwise correlation functions and domain length scales.

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I. INTRODUCTION

There has been a great deal of interest in problems of phase-ordering dynamics in recent years. A prototypical problem in this area is the phase-separation kinetics of a homogeneous binary AB mixture that has been rendered thermodynamically unstable by a rapid quench below the miscibility curve. If the quenched mixture is spontaneously unstable, the evolution kinetics is usually referred to as spinodal decomposition (SD). During SD there is an emergence and growth of A -rich and B -rich domains, characterized by a single time-dependent length scale $L(t)$. This has important consequences, e.g., the correlation function of the order parameter field exhibits the scaling form $C(r,t) = f[r/L(t)]$, where $f(x)$ is a scaling function. We now have a good understanding of the kinetics of phase separation in the bulk and there are several good reviews of these problems [1–4].

Let us consider the equilibrium behavior of an immiscible AB mixture in contact with a surface S . Typically, the surface has a preferential attraction for one of the components of the mixture, say, A . Let γ_A and γ_B be the surface tensions between the A -rich and B -rich phases and S , respectively, and let σ be the surface tension between the A -rich and B -rich phases. We focus on a semi-infinite geometry for simplicity. Then the contact angle θ between the AB interface and the surface can be obtained from Young's equation [5]

$$\sigma \cos\theta = \gamma_B - \gamma_A. \quad (1)$$

When $\gamma_B - \gamma_A > \sigma$, the A -rich phase covers the surface in a completely wet (CW) morphology. However, for $\gamma_B - \gamma_A < \sigma$ both phases are in contact with the surface, resulting in a partially wet (PW) equilibrium morphology.

We have had a long-standing interest in the kinetics of binary mixtures at surfaces. Consider a homogeneous AB mixture at high temperatures. This mixture is kept in contact with a surface that prefers A . The system is quenched deep below the miscibility curve at time $t = 0$. Then the system becomes unstable to phase separation and decomposes into A -rich and B -rich domains. The surface is simultaneously wetted by A . The interplay of these two dynamical processes, i.e., wetting and phase separation, is referred to as surface-directed spinodal decomposition (SDSD) or surface-directed phase separation [6–23]. These processes have important tech-

nological applications, including the fabrication of nanoscale patterns and multilayered structures.

With some exceptions [24,25], most available studies of SDSD do not take into account hydrodynamic effects, i.e., the growth of bulk domains, and the wetting layer is governed by diffusion. However, many important experiments in this area involve fluid or polymer mixtures, where fluid velocity fields play a substantial role in determining physical properties. Hydrodynamic effects alter the late-stage dynamics of phase separation in a drastic manner, both without surfaces [1,2,26–29] and with surfaces [24,25]. In this paper we have undertaken extensive molecular dynamics (MD) simulations to investigate the effects of hydrodynamics on the late-stage dynamics of SDSD. We observe a clear crossover from a diffusive regime to a hydrodynamic regime in the growth law for the wetting layer. A preliminary account of our results was published in a recent Letter [30].

This paper is structured as follows. In Sec. II we describe the details of our MD simulations. Section III presents a brief review of the bulk phase-separation kinetics and domain growth laws and then discusses phase separation at surfaces. Detailed MD results are presented in Sec. IV. We end with a summary and discussion of our results in Sec. V.

II. DETAILS OF SIMULATIONS

We employ standard MD techniques for our simulations [31,32]. The model is similar to that used in our earlier studies of mixtures at surfaces [20,33]. We consider a binary fluid mixture AB consisting of N_A number of A atoms and N_B number of B atoms (with $N_A = N_B$), confined in a box of volume $L_w \times L_w \times D$. While periodic boundary conditions are maintained in the x and y directions, walls or surfaces are introduced in the z direction at $z = 0$ and D . The interaction between two atoms of species i and j separated by a distance r is given by the Lennard-Jones (LJ) potential

$$u_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad i, j = A, B. \quad (2)$$

Here the LJ energy parameters are set as $\epsilon_{AA} = \epsilon_{BB} = 2\epsilon_{AB} = \epsilon$. The details of the equilibrium phase behavior for this potential are well studied [34–36]. If we express all lengths in terms of the LJ diameter σ , masses in units of m ($m_A = m_B = m$),

and energies in terms of ϵ , the natural time unit is

$$t_0 = \sqrt{\frac{m\sigma^2}{48\epsilon}}. \quad (3)$$

Setting $\sigma = 1$, $m = 1$, and $\epsilon = 1$ gives $t_0 = 1/\sqrt{48}$. The potential in Eq. (2) is cut off at $r_c = 2.5\sigma$ to enhance computational speed. To remove the discontinuities in the potential and force at $r = r_c$, we invoke the shifted-potential and shifted-force potential corrections to the potential in Eq. (2) [31].

For the potential between the walls and the fluid particles, we consider an integrated LJ potential ($\alpha = A, B$)

$$u_w(z) = \frac{2\pi n\sigma^3}{3} \left[\frac{2\epsilon_r}{15} \left(\frac{\sigma}{z'} \right)^9 - \delta_\alpha \epsilon_a \left(\frac{\sigma}{z'} \right)^3 \right]. \quad (4)$$

Here n is the reference density of the bulk fluid and ϵ_r and ϵ_a are the energy scales for the repulsive and attractive parts of the interaction. We set $\delta_A = 1$ and $\delta_B = 0$ for the wall at $z = 0$. Thus A particles are attracted at large distances and repelled at short distances, whereas B particles experience only repulsion. For the wall at $z = D$, we choose $\delta_A = 0$ and $\delta_B = 0$, so there is only a repulsion for both A and B particles. Furthermore, we have $z' = z + \sigma/2$ for the wall at $z = 0$ and $z' = D + \sigma/2 - z$ for the wall at $z = D$. We notice that this simplified potential incorporates the effect of a semi-infinite geometry (the generalization to any other geometry is straightforward). However, it does not take into account the surface structure in the xy plane.

The fluid has $N = N_A + N_B$ particles and the fluid density is $n = N/L_w^2 D = 1$. In our simulations, we chose $L_w = 48$ and $D = 48$ ($N = 110\,592$ particles). In recent studies [37,38] it has been demonstrated that in the bulk phase separation, the scaling laws for the growth of the average domain size is unaffected until the latter reaches almost the size of the system. In the present problem applications of periodic boundary conditions in the lateral directions make the problem of domain growth in these directions equivalent to the case of bulk phase separation. Considering these facts and noting that within the time scale of our simulations the average lateral size of the domains is at most 5 atomic diameters (see later), $L_w = 48$ is large enough to avoid any undesirable effects due to finite size of the systems. For the similar issue in the z direction, we note that for the present choice of parameters one has a first-order wetting transition [30]. In such a situation the equilibrium thickness of the wetting layer is expected to be finite and should not create difficulty as encountered in critical transitions. Nevertheless, we have checked our results for various values of D and settled on $D = 48$.

The statistical quantities presented here were obtained as averages over 50 independent runs. We performed simulations on the fluid for the surface potential Eq. (4) with $\epsilon_a = 0.1$ and 0.6 , while $\epsilon_r = 0.5$. We find that $\epsilon_a = 0.1$ corresponds to a PW morphology, while $\epsilon_a = 0.6$ yields a CW morphology [39]. The quench temperature is $T = 1.0 \simeq 0.7T_c$ (bulk $T_c \simeq 1.423$) [35,36] and is maintained by the Nosé-Hoover thermostat, which preserves hydrodynamics [28,29,40]. The homogeneous initial state of the fluid mixture is prepared from a short run at high T ($\gg T_c$), with periodic boundary conditions

imposed in all directions. Finally, Newton's equations of motion are integrated numerically using the Verlet velocity algorithm [40], with a time step $\Delta t = 0.07$ in LJ units. The computation was performed on single processors with a CPU speed of 2.6 GHz. On average, a run length of unity (in LJ unit) was completed in 5.86 min.

We undertook extensive MD simulations to study the time-dependent morphology that arises during surface-directed phase separation. We characterized the morphology via layer-wise correlation functions, structure factors, and length scales. We also computed laterally averaged order parameter profiles and their various properties, e.g., the surface value of the order parameter and zero crossings. Before presenting these quantities, it is useful to summarize theoretical results in this context.

III. THEORETICAL BACKGROUND

A. Kinetics of phase separation in the bulk

The coarsening domains have a characteristic length scale $L(t)$, which grows with time. For pure and isotropic systems, $L(t) \sim t^\theta$, where the growth exponent θ depends on the conservation laws, the nature of defects that drive the evolution, and the relevance of hydrodynamic flow fields.

First, we discuss the domain growth laws that arise in bulk phase-separating systems [41–46]. For diffusive dynamics, the order parameter satisfies the Cahn-Hilliard (CH) equation. In dimensionless variables this has the form [1]

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = \nabla^2 \left(-\psi + \psi^3 - \frac{1}{2} \nabla^2 \psi \right), \quad (5)$$

where the order parameter $\psi(\vec{r}, t)$ is proportional to the AB density difference at space point \vec{r} and time t . Lifshitz and Slyozov [41] considered the diffusion-driven growth of a droplet of the minority phase in a supersaturated background of the majority phase. The Lifshitz-Slyozov (LS) mechanism leads to the growth law $L(t) \sim t^{1/3}$ in $d \geq 2$. Huse [46] argued that this law is also valid for spinodal decomposition in mixtures with approximately equal fractions of the two components. Typically, for a domain of size L , the chemical potential on its surface is $\mu \sim \sigma/L$, where σ is the surface tension. Then the current is $D|\nabla\mu| \sim D\sigma/L^2$, where D is the diffusion constant. Therefore, the domain size grows as $dL/dt \sim D\sigma/L^2$, or $L(t) \sim (D\sigma t)^{1/3}$.

We now consider the segregation of binary fluids, where the hydrodynamic flow field provides an additional mechanism for the transport of material [1–4]. Hydrodynamic effects can be incorporated into the CH model by including a velocity field that satisfies the Navier-Stokes equation: The resultant coupled equations are termed model H [47]. The growth dynamics is diffusion limited at early times, as in the case of binary alloys. However, one finds a crossover to a hydrodynamic growth regime, where convection assists in the rapid transportation of material along the domain boundaries [42,43]. The growth laws for different regimes are summarized

as follows [1]:

$$L(t) \sim \begin{cases} (D\sigma t)^{1/3}, & L \ll (D\eta)^{1/2} & \text{(diffusive regime)} \\ \frac{\sigma t}{\eta}, & (D\eta)^{1/2} \ll L \ll \frac{\eta^2}{\rho\sigma} & \text{(viscous hydrodynamic regime)} \\ \left(\frac{\sigma t^2}{\rho}\right)^{1/3}, & \frac{\eta^2}{\rho\sigma} \ll L & \text{(inertial hydrodynamic regime).} \end{cases} \quad (6)$$

In Eq. (6), η and ρ denote the viscosity and density of the fluid, respectively.

B. Kinetics of phase separation at wetting surfaces

We briefly discuss phase-separation kinetics at wetting surfaces [18,23]. For the diffusive case, the order parameter satisfies the CH equation in the bulk:

$$\frac{\partial}{\partial t} \psi(\vec{\rho}, z, t) = \nabla^2 \left[-\psi + \psi^3 - \frac{1}{2} \nabla^2 \psi + V(z) \right], \quad z > 0. \quad (7)$$

In Eq. (7) we have designated $\vec{r} \equiv (\vec{\rho}, z)$, where $\vec{\rho}$ and z denote coordinates parallel and perpendicular to the surface (located at $z = 0$), respectively. The surface potential $V(z)$ is chosen such that the surface preferentially attracts A .

Equation (7) must be supplemented by two boundary conditions at $z = 0$ [11,18], as it is a fourth-order partial differential equation. Now, since the surface value of the order parameter is not conserved, we assume a nonconserved relaxational kinetics for this quantity:

$$\begin{aligned} \frac{\partial}{\partial t} \psi(\vec{\rho}, 0, t) &= h_1 + g\psi(\vec{\rho}, 0, t) + \gamma \frac{\partial}{\partial z} \psi(\vec{\rho}, z, t) \Big|_{z=0} \\ &+ \tilde{\gamma} \nabla_{\parallel}^2 \psi(\vec{\rho}, 0, t). \end{aligned} \quad (8)$$

In Eq. (8), $h_1 = -V(0)$; g , γ , and $\tilde{\gamma}$ are phenomenological parameters; and ∇_{\parallel}^2 denotes the in-plane Laplacian. Next we implement a zero-current boundary condition at the surface, which enforces the conservation of the order parameter:

$$0 = \frac{\partial}{\partial z} \left[-\psi + \psi^3 - \frac{1}{2} \nabla^2 \psi + V(z) \right] \Big|_{z=0}. \quad (9)$$

Equations (7)–(9) describe the kinetics of SDSD with diffusive dynamics. This is appropriate for phase separation in solid mixtures or the early stages of segregation in polymer blends. However, most experiments involve fluid mixtures, where hydrodynamics plays an important role in the intermediate and late stages of phase separation. At a phenomenological level, hydrodynamic effects can be incorporated via the Navier-Stokes equation for the velocity field [47]. This must be supplemented by appropriate boundary conditions at the surfaces [25]. Alternatively, we can consider molecular models of fluid mixtures at a surface, in which the fluid velocity field is naturally included. We adopt the latter strategy in this paper and study SDSD in fluid mixtures via MD simulations.

Let us briefly discuss the growth laws that arise in SDSD. At early times, the wetting-layer growth is driven by the diffusion of A particles from bulk domains of size $L \sim (\sigma t)^{1/3}$ (with $\mu \sim \sigma/L$) to the flat surface layer of size $\simeq \infty$ (with $\mu \simeq 0$). Therefore, neglecting the contribution due to the surface

potential at very early times [17], we obtain

$$\frac{dR_1}{dt} \sim \frac{\sigma}{Lh} \sim \frac{\sigma}{LR_1}, \quad (10)$$

where $h \sim R_1$ is the thickness of the depletion layer. The LS growth law for the wetting-layer thickness [$R_1 \sim (\sigma t)^{1/3}$] can be readily obtained from Eq. (10). At later times, R_1 shows a rapid growth due to the establishment of contact between the bulk tubes and the wetting layer. Then the wetting component is pumped hydrodynamically to the surface. The subsequent growth dynamics is similar to that in segregation of fluids. We expect $R_1(t) \sim t$ in the viscous hydrodynamic regime, followed by a crossover to $R_1(t) \sim t^{2/3}$ in the inertial hydrodynamic regime.

IV. DETAILED NUMERICAL RESULTS

In this section we present results from our MD simulations. The details of these have been described in Sec. II. First, we focus on domain morphologies and laterally averaged profiles for the CW case. In Fig. 1 we show evolution snapshots and their yz cross sections for SDSD in a binary AB fluid mixture at different times. The surface field strengths are

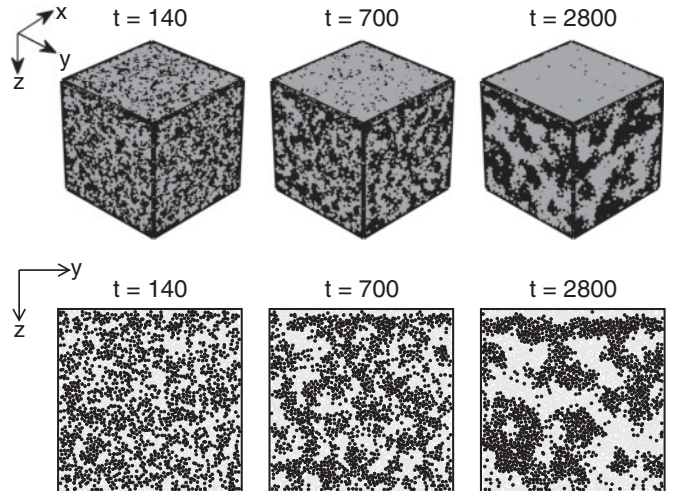


FIG. 1. Evolution snapshots (top frames) for surface-directed spinodal decomposition in a binary AB Lennard-Jones mixture, which is confined in a box of size $L_w^2 \times D$, with $L_w = 48$ and $D = 48$. An impenetrable surface (located at $z = 0$) attracts the A particles (marked gray). The surface field strength is given by $\epsilon_a = 0.6$ and $\epsilon_r = 0.5$ in Eq. (4), which corresponds to a completely wet morphology in equilibrium. The temperature is $T = 1.0 \simeq 0.7 T_c$ (bulk $T_c = 1.423$). The other simulation details are provided in the text. The B particles are marked black. The bottom frames show the yz cross sections of the top frames at $x = 0$.

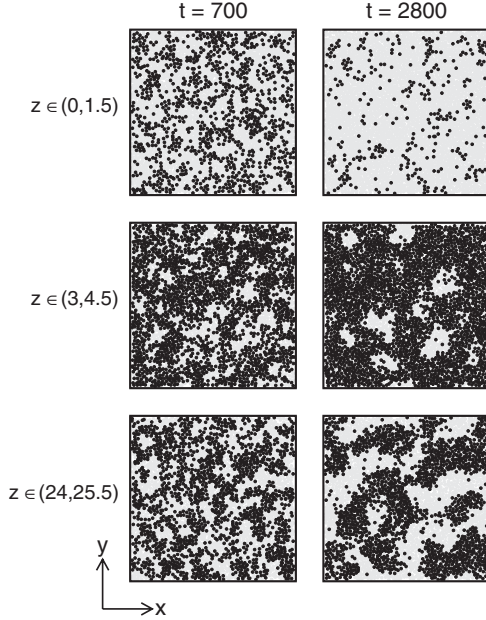


FIG. 2. Cross-section slices of size $L_w^2 \times 1.5\sigma$ for the evolution shown in Fig. 1 at $t = 700$ and 2800 MD units. The slices show all A atoms (marked in gray) and all B atoms (marked in black) lying in the intervals $z \in (0, 1.5)$ (top frames), $z \in (3, 4.5)$ (middle frames), and $z \in (24, 25.5)$ (bottom frames).

$\epsilon_r = 0.5$ and $\epsilon_a = 0.6$ in Eq. (4), which correspond to a CW morphology in equilibrium. An A -rich layer develops at the surface ($z = 0$), resulting in SDSD waves that propagate into the bulk. Consequently, the surface exhibits a multilayered morphology, i.e., wetting layer followed by depletion layer, etc. The snapshots (and their cross sections in the bottom frames) clearly show that only A particles are at the surface, as expected for a CW morphology.

In Fig. 2 we show cross sections in the xy plane for the evolution snapshots in Fig. 1. The surface layer (shown in the top frames at $t = 700$ and 2800) has almost no B particles. In the middle frames we notice that there is a surplus of B atoms due to the migration of A particles to the surface. (This is confirmed by the laterally averaged profiles, shown in Fig. 3.) The bottom frames show the usual segregation morphologies in the bulk (which correspond to the region $z \in [24, 25.5]$), which is unaffected by the SDSD waves at these simulation times (see Fig. 3).

Depth-profiling techniques in experiments do not have much lateral resolution and yield only laterally averaged order parameter profiles $\psi_{av}(z, t)$ vs z [10]. The numerical counterpart of these profiles is obtained by averaging $\psi(\vec{\rho}, z, t)$ in the x and y directions and then further averaging over 50 independent runs. The order parameter is defined from the local densities n_A and n_B as

$$\psi(\vec{r}, t) = \frac{n_A - n_B}{n_A + n_B}. \quad (11)$$

In Fig. 3 we show the depth profiles for the evolution depicted in Fig. 1. Figure 3 clarifies the nature of the multilayered morphology seen in SDSD. In the bulk the SDSD wave vectors are randomly oriented, which results in $\psi_{av}(z, t) \simeq 0$ due to the

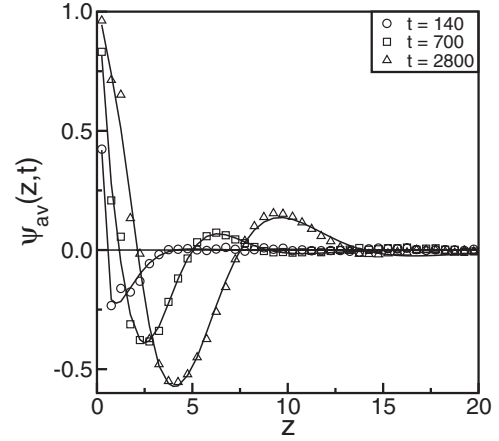


FIG. 3. Laterally averaged order parameter profiles for the evolution shown in Fig. 1 at $t = 140$, 700 , and 2800 MD units. The solid lines through the data points are guides to the eye.

averaging procedure. However, the averaged profiles show a systematic oscillatory behavior at the surface.

Let us next examine the velocity field at the surface and in the bulk. In Fig. 4 we show the (v_x, v_y) field in the xy planes used in Fig. 2. The snapshots shown in Fig. 4 are obtained by coarse graining the velocities in overlapping boxes of size $(4.5\sigma)^3$. These boxes are centered on cubes of size $(1.5\sigma)^3$ and we show the (v_x, v_y) field for these cubes. We make the following observations concerning Fig. 4. (i) The velocity field

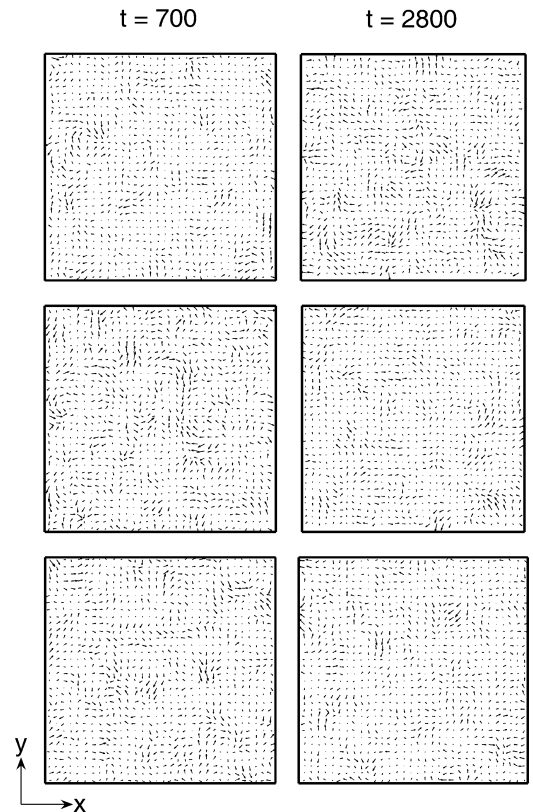


FIG. 4. Analogous to Fig. 2, but for the velocity field (v_x, v_y) in the xy plane. The velocities are coarse grained as described in the text.

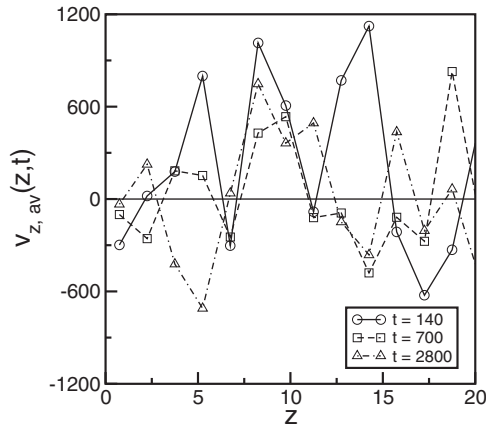


FIG. 5. Laterally averaged v_z profiles for the evolution shown in Fig. 1 at $t = 140, 700,$ and 2800 MD units.

is characterized by vortices and antivortices, but these do not show much coarsening with time (compare the snapshots at times $t = 700$ and 2800 for different values of z). (ii) There are no significant morphological differences between the velocity fields at the surface (top frames of Fig. 4) and in the bulk (bottom frames of Fig. 4). This is confirmed by comparing the corresponding correlation functions; for brevity, we do not present these here. While this observation is consistent with the MD study of bulk phase separation [28,29], this is at variance with the simulation of model H where annihilation of these vortices and antivortices was observed. Even though a possible reason for observing such coarsening could be an artifact of the latter model itself, it would be premature to make any such definitive comment since the length scales accessed by the two approaches differ hugely. Thus a more systematic study is required to resolve this interesting issue.

It is relevant to ask whether the depth profiles of the velocity field show any systematic behavior (as in Fig. 3). In Fig. 5 we plot $v_{z,av}(z,t)$ vs z for $t = 140, 700,$ and 2800 . The procedure for calculating the laterally averaged velocity field is as follows: In each layer of thickness 1.5σ (in the z direction), we sum up the z components of the velocities for all particles. A similar plot for the concentration field would show oscillations with increasing amplitude and wavelength as time progresses, thus reflecting the surface-induced coarsening. Clearly, the absence of such a systematic feature in the velocity field is reflective of no growth of ordering in this field.

Next we turn our attention to the morphologies and profiles for the PW case. The evolution snapshots and their yz cross sections for the PW morphology are shown in Fig. 6. In this case we set $\epsilon_r = 0.5$ and $\epsilon_a = 0.1$ in Eq. (4). As in the CW case, we again observe the usual phase-separation morphologies in the bulk; however, in this case, both A and B particles are present at the surface.

Figure 7 shows the cross sections in the xy plane, corresponding to the evolution in Fig. 6. At early times ($t = 700$, top frame) approximately equal numbers of A and B particles are present at the surface; however, there is a surplus of A atoms at late times ($t = 2800$, top frame), as expected in the PW morphology. In the middle frames, we see more B particles, as A atoms have migrated to the surface. The laterally averaged profiles in Fig. 8 show that $z \in [3,4.5]$ (corresponding to

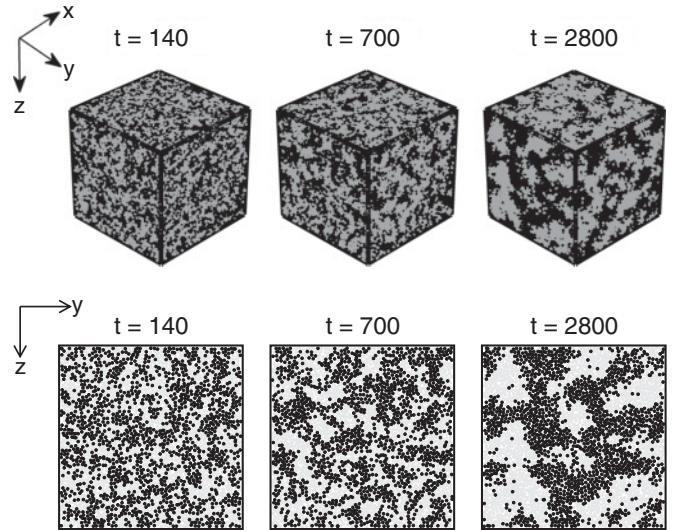


FIG. 6. Analogous to Fig. 1, but for the case with $\epsilon_a = 0.1$ and $\epsilon_r = 0.5$. These parameters correspond to a partially wet morphology in equilibrium.

the middle frames in Fig. 7) lies in the depletion layer for both $t = 700$ and 2800 . The bottom frames in Fig. 7 show the segregation kinetics in the bulk.

We plot $\psi_{av}(z,t)$ vs z in Fig. 8, corresponding to the PW evolution in Fig. 6. A behavior similar to the CW morphology (cf. Fig. 3) is seen in this case too. However, notice that the degree of surface enrichment (and depletion adjacent to the surface) is much less in Fig. 8.

We have also studied the morphology of the velocity field in the PW case. The features are analogous to those in Figs. 4 and 5 for the CW case and we do not show these results here.

We now examine some quantitative properties of the depth profiles in Figs. 3 and 8. Figure 9 shows the time dependence of the surface value of the order parameter for the CW and PW

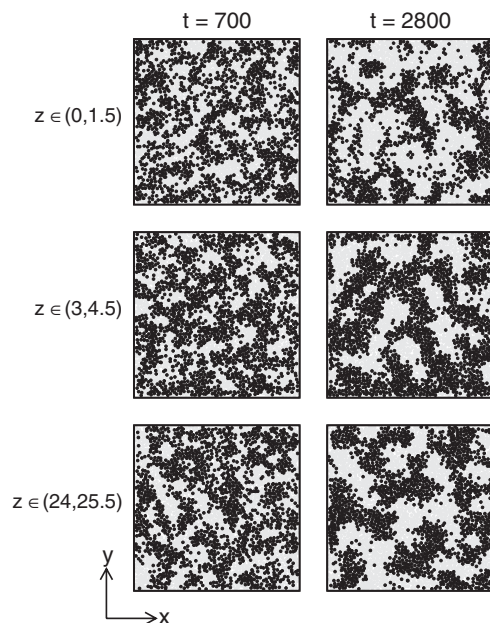


FIG. 7. Analogous to Fig. 2, but for the evolution shown in Fig. 6.

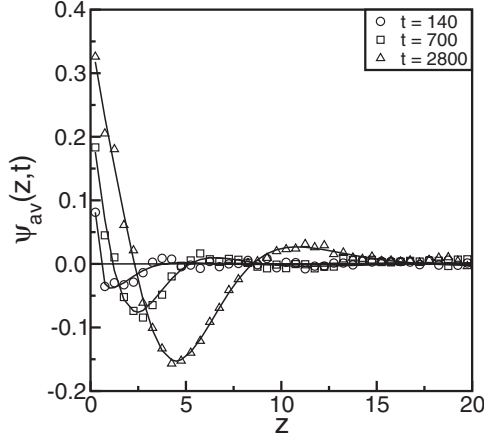


FIG. 8. Analogous to Fig. 3, but corresponding to the evolution shown in Fig. 6.

cases. We plot $\psi_{av}(0,\infty) - \psi_{av}(0,t)$ vs t^{-1} , demonstrating that $\psi_{av}(0,t)$ saturates linearly to its asymptotic value $\psi_{av}(0,\infty)$ for the CW case (with $\epsilon_a = 0.6$):

$$\psi_{av}(0,t) \simeq \psi_{av}(0,\infty) - \frac{A}{t} + \dots, \quad (12)$$

where A is a constant. Notice that the asymptotic value $\psi_{av}(0,\infty)$ is estimated by extrapolation of the data for $\psi_{av}(0,t)$ vs t . The corresponding behavior for the PW case (with $\epsilon_a = 0.1$) is not so clear. However, our results suggest that the PW case also saturates linearly at long times.

The evolution of the SDSA profiles in Figs. 3 and 8 is characterized by the zero crossings of $\psi_{av}(z,t)$. The quantity $R_1(t)$ denotes the first zero and measures the wetting-layer thickness. Figure 10 plots $R_1(t)$ vs t for the CW and PW cases shown in Figs. 3 and 8. This plot shows a power-law behavior for the growth dynamics, $R_1(t) \sim t^\theta$, but there is a distinct crossover in the growth exponent. For $t \leq t_c \simeq 2000$ we have $\theta \simeq 1/3$, in conformity with the LS mechanism for

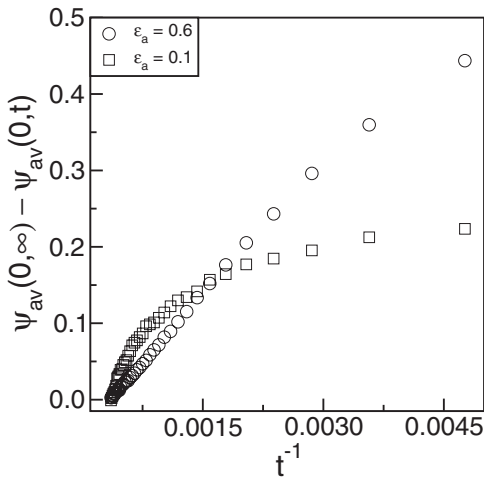


FIG. 9. Time dependence of the surface value of the order parameter for the CW and PW profiles in Figs. 3 and 8, respectively. We plot $\psi_{av}(0,\infty) - \psi_{av}(0,t)$ vs t^{-1} .

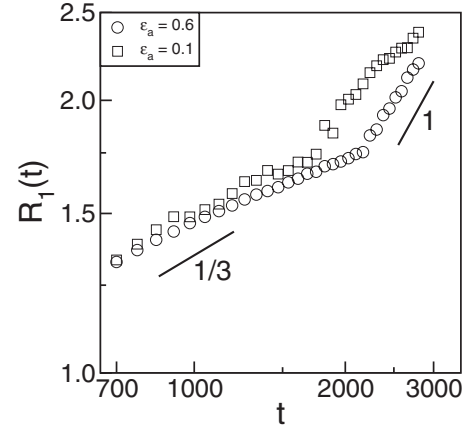


FIG. 10. Time dependence of the wetting-layer thickness $R_1(t)$ of the CW and PW profiles on a log-log scale. The straight lines have slopes $1/3$ and 1 , corresponding to the diffusive regime and the viscous hydrodynamic regime, respectively.

diffusive growth. However, for $t \geq t_c$ we observe a much more rapid growth with $\theta \simeq 1$, corresponding to the viscous hydrodynamic regime. We make the following observations regarding Fig. 10.

(i) The crossover time is consistent with the observation of a $1/3 \rightarrow 1$ crossover (at $t_c \simeq 2000$) in bulk MD simulations by Ahmad *et al.* [28,29]. Those authors used a similar model, but without surface interactions.

(ii) The crossover in the CW case is much sharper than in the PW case. In the CW case bulk tubes establish contact with

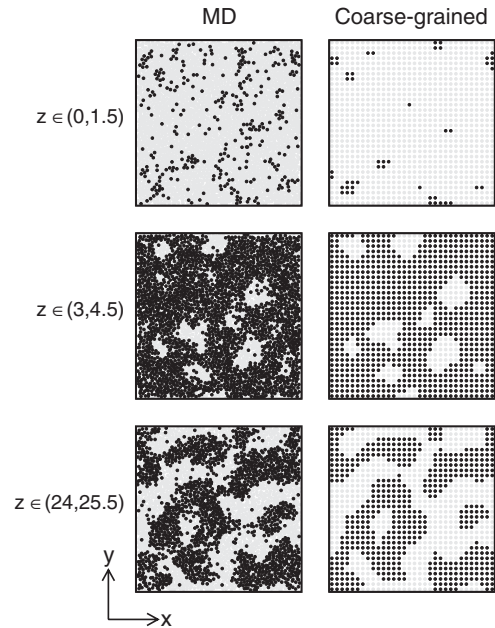


FIG. 11. Cross sections of the SDSA snapshots (frames on left) at $t = 2800$ shown in Fig. 2. The cross sections show all A atoms (marked gray) and all B atoms (marked black) lying in the intervals $z \in (0, 1.5)$ (top frames), $z \in (3, 4.5)$ (middle frames), and $z \in (24, 25.5)$ (bottom frames). The frames on the right show coarse-grained versions of the MD snapshots. The coarse-graining procedure is described in the text.

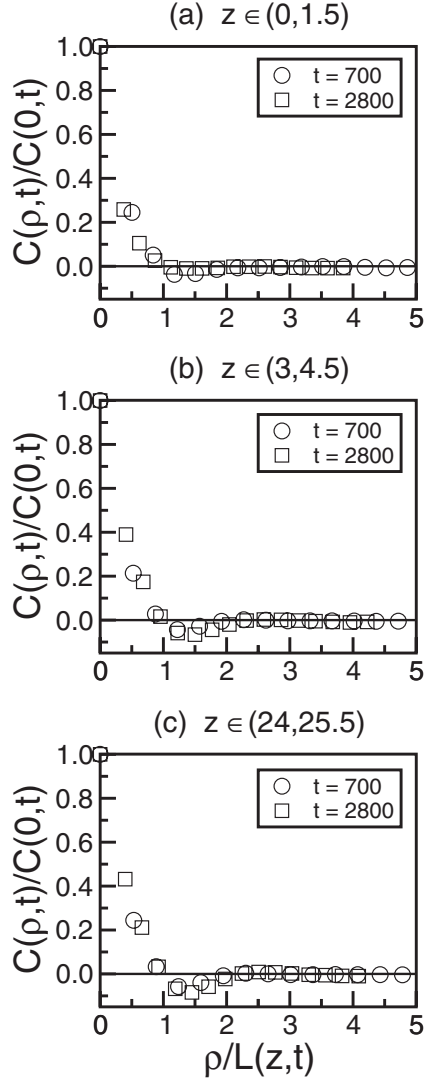


FIG. 12. Scaling plot of the layerwise correlation functions for the CW evolution depicted in Fig. 1. We plot $C(\rho, t)/C(0, t)$ vs $\rho/L(z, t)$ for $t = 700$ and 2800 with (a) $z \in (0, 1.5)$, (b) $z \in (3, 4.5)$, and (c) $z \in (24, 25.5)$.

a flat wetting layer and rapidly drain into it. In the PW case the surface morphology consists of semidroplets and the pressure differences from the bulk tubes are less marked.

(iii) We can go up to $t \simeq 3000$ for these system sizes ($L_w = 48$ and $D = 48$). Beyond this time the system encounters finite-size effects due to the lateral domain size becoming an appreciable fraction of the system size L_w . Presently, our computational constraints do not allow us to access the inertial hydrodynamic regime (with $\theta = 2/3$) via MD simulations [28,29]. However, our results for the wetting-layer dynamics show the viscous hydrodynamic regime, though in a limited time window.

Before concluding this section we discuss some other quantitative features of the domain morphologies. We present results for the CW case only; the PW results are analogous. First, we focus on the layerwise correlation function, which characterizes the domain morphology. This is

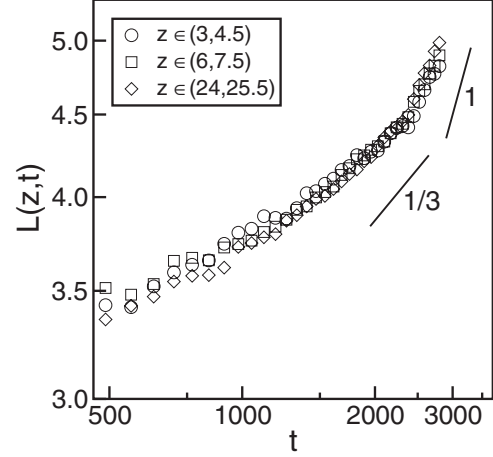


FIG. 13. Time dependence of the lateral domain size for the evolution depicted in Fig. 1. We plot $L(z, t)$ vs t on a log-log scale for various values of z . The solid lines have slopes $1/3$ (diffusive regime) and 1 (viscous hydrodynamic regime).

defined as [12]

$$C_{\parallel}(\vec{\rho}, z, t) = L_w^{-2} \int d\vec{\sigma} [\langle \psi(\vec{\sigma}, z, t) \psi(\vec{\sigma} + \vec{\rho}, z, t) \rangle - \langle \psi(\vec{\sigma}, z, t) \rangle \langle \psi(\vec{\sigma} + \vec{\rho}, z, t) \rangle], \quad (13)$$

where the angular brackets denote statistical averaging over independent runs. We denote $C_{\parallel}(\vec{\rho}, z, t)$ as $C(\vec{\rho}, t)$ in the following discussion for convenience. Since the system is isotropic in the x and y directions, C is independent of the direction of $\vec{\rho}$. We can define the z -dependent lateral length scale $L_{\parallel}(z, t) \equiv L(z, t)$ from the half decay of $C(\rho, t)$ [12]:

$$C(\rho = L, t) = \frac{1}{2} C(0, t). \quad (14)$$

To obtain the correlation function, etc., a coarse-graining procedure is employed to remove the noise. This is similar to a numerical renormalization group technique described in Ref. [48]. We divide our system into small boxes of size $\sigma^2 \times 1.5\sigma$. We count the total number of A and B particles in each box and its nearest neighbors. If there are more particles of A than B in the box and its neighbors, we assign a spin value $S = 1$ to that box. On the other hand, the box is given a spin value $S = -1$ when there are more B particles than A particles. Furthermore, we assign 1 or -1 to a box randomly, when equal numbers of A and B particles are present.

The results of this coarse-graining procedure are shown in Fig. 11. In the frames on the left, we reproduce the xy cross sections of the SDSD snapshots at $t = 2800$ in Fig. 2. The frames on the right show the corresponding coarse-grained pictures. Figure 11 clearly demonstrates the elimination of fluctuations in our coarse-grained snapshots while preserving the important morphological features.

In Fig. 12 we plot the normalized correlation function $C(\rho, t)/C(0, t)$ (computed from the coarse-grained spin variable) vs $\rho/L(z, t)$ for three different layers, as indicated in the figure. The surface layer [$z \in (0, 1.5)$] has few inhomogeneities and shows a corresponding lack of structure in the correlation function. [Notice that a state with $S_i = 1 \forall i$ has $C(\rho) = 0$ from our definition in Eq. (13).] The layer at $z \in (3, 4.5)$ lies in the depletion region for $t = 700$ and 2800 , as seen from

the laterally averaged profiles in Fig. 3. The corresponding correlation functions (middle frame of Fig. 12) show scaling behavior. The bottom frame in Fig. 12 corresponds to a bicontinuous bulk morphology (see bottom frames of Fig. 11).

Finally, we focus on the time dependence of the lateral domain size $L(z,t)$. In Fig. 13 we plot $L(z,t)$ vs t for three different layers, excluding the surface layer. (As evident from the top frames of Fig. 11, there is no characteristic domain scale associated with the surface layer.) We find that $L(z,t)$ grows as a power law with time ($L \sim t^\theta$), but there is a crossover in the growth exponent. The early-time dynamics ($t \leq t_c$) is consistent with the expected diffusive LS growth law with $\theta \simeq 1/3$ [1–4]. However, there is a much more rapid growth at late times ($t \geq t_c$) with $\theta \simeq 1$. Notice that the crossover time ($t_c \simeq 2000$) is consistent with the crossover time for the growth dynamics of the wetting layer.

V. CONCLUSION

Let us conclude this paper with a brief summary and discussion of our results. We have studied surface-directed spinodal decomposition in an unstable homogeneous binary AB mixture at a wetting surface S . Depending on the relative values of the surface tensions between A , B , and S , the equilibrium morphology can be either completely wet or partially wet. Most experiments on SDSD have been performed on polymer blends, fluid mixtures, etc., where hydrodynamic effects play an important role in the intermediate and late stages of phase separation. However, there have been very few numerical investigations of SDSD with hydrodynamics.

We undertook comprehensive molecular dynamics simulations to study the kinetics of SDSD in this paper. The MD simulations were performed with a Nosé-Hoover thermostat,

which naturally incorporates hydrodynamic effects. In both CW and PW cases the surface becomes the origin of SDSD waves, which propagate into the bulk. The typical SDSD profile consists of a multilayered morphology, i.e., a wetting layer followed by a depletion layer, etc. We are interested in understanding the role of hydrodynamics in driving the growth of the bulk domain size and the wetting layer. At early times the wetting layer grows diffusively with time ($R_1 \sim t^{1/3}$). However, there is a crossover to a convective regime and the late-stage dynamics is $R_1 \sim t$. There is also a corresponding crossover in the growth dynamics of the bulk domain size $L(t)$. Due to computational limitations, our MD simulations are as yet unable to access the inertial hydrodynamic regime (with $L, R_1 \sim t^{2/3}$) in either the bulk or the wetting-layer kinetics.

Our findings have significant implications for experiments on SDSD. It is understood that the fluid phase separation is a much more complex phenomenon than that in solid mixtures. We hope that this work will provoke fresh experiments on this problem.

Note that it would be interesting to study the dependence of this nonequilibrium dynamics on the quench depth. As a passing remark we mention that due to the vanishing of surface tension, which provides the driving force, as one approaches the critical temperature, the bulk phase separation gets slower [29]. Even though we expect a similar temperature dependence in the present case, the situation is much more complex here due to several interfacial tensions dictating the phenomena.

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